## Cation exchange-driven Li isotope fractionation during water-rock interaction: a case study of groundwater in the Ordos basin, China

TAO-TAO JI<sup>1</sup>, XIAO-WEI JIANG<sup>1</sup>, LONG-FEI GOU<sup>2</sup>, ZHANGDONG JIN<sup>2</sup>, HONG ZHANG<sup>1</sup>, WAN LI<sup>1</sup>, GUILIN HAN<sup>3</sup>, HUAMING GUO<sup>1</sup>, XU-SHENG WANG<sup>1</sup>

<sup>1</sup> MOE Key Laboratory of Groundwater Circulation and Environmental Evolution, China University of Geosciences, Beijing 100083, China. Corresponding email: jxw@cugb.edu.cn

<sup>2</sup> State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710061, China.

<sup>3</sup> Institute of Earth Sciences, China University of Geosciences, Beijing 100083, China.

Previous work showed that the Li isotopic compositions of natural water are primarily controlled by silicate dissolution and clay formation. Silicate dissolution was suggested to result in insignificant Li isotope fractionation, while the formation of secondary minerals could release heavy Li into water. However, the role of cation exchange during water-rock interaction, which is a common hydrological process in terrestrial water systems, on Li isotope fractioantion was often ignored and rarely explored in natural water in previous studies. Here, we reported the Li isotopic compositions of groundwater from a Cretaceous sandstone aquifer in the Ordos Basin, China. The samples from the discharge area show negative correlations of Mg with Na and Li, indicating Li-Mg and Na-Mg exchange between groundwater and sandstone. Their  $\delta^7$ Li values range from 17.1‰ to 24.9‰ and are positively correlated with Li concentrations, which is contrary to the negative trend of  $\delta^7 Li$ with Li concentrations induced by clay formation but most likely reflects incorporation of variable proportions of exchangeable Li from sandstone into groundwater during Li-Mg cation exchange process. An maximum  $\alpha_{sandstone-water}$  (Li isotope fractionation factor between sandstone and water) of 0.9774 was deduced from our study based on a mixing model, which lies within the range of experimentally documented isotope fractionation factors. Therefore, in addition to clay formation and silicate dissolution, cation exchange during water-rock interaction may be another important process that is responsible for Li isotope variations in groundwater or river water